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SiC-Based Gas Sensor Development

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Abstract: Silicon carbide based Schottky diode gas sensors are being developed for applications such as emission measurements and leak detection. The effects of the geometry of the tin oxide film in a Pd/SnO_2/SiC structure will be discussed as well as improvements in packaging SiC-based sensors. It is concluded that there is considerable versatility in the formation of SiC-based Schottky diode gas sensing structures which will potentially allow the fabrication of a SiC-based gas sensor array for a variety of gases and temperatures.

1.0 Introduction

Silicon carbide-based gas sensors are of considerable interest since they can be operated at high temperatures and detect gases, such as hydrocarbons (C_xH_y) and nitrogen oxides (NO_x), which are important in various applications such as emission monitoring and leak detection. Our development of SiC-based gas sensors has centered on investigations of gas sensitive Schottky diodes. The major advantage of a Schottky diode in gas sensing applications is its high sensitivity. While a simple palladium (Pd) on SiC (Pd/SiC) Schottky diode structure has the advantage of high sensitivity, these sensors drift with extended heating at high (400 °C) temperature [1]. Efforts are underway to stabilize the Schottky sensor structure for long-term, high temperature operation [2].

One approach incorporates chemically reactive materials such as metal oxides into a SiC-based metal-insulator-semiconductor (MIS) Schottky diode structure. Unlike Si-based electronics, SiC-based devices can be operated at high enough temperatures for these materials, e.g. tin oxide (SnO_2), to be reactive to C_xH_y and NO_x. This results in a metal-reactive insulator-semiconductor (MRIS) gas sensor structure. Potential advantages of this structure include increased sensor sensitivity and stability. Varying the reactive insulator composition can vary sensor selectivity to various gas species. We previously demonstrated this structure with SnO_2 as the reactive insulator and compared the reactive insulator sensor response to that of a Pd/SiC structure on the same chip (Figure 1a) [2]. The MRIS sensor showed improved stability and different responses than the Pd/SiC sensor.

This approach, combined with metal-alloys directly on SiC [2], potentially yields wide flexibility in the design and operational capabilities of SiC-based gas sensing Schottky diodes. Various reactive oxides and metal alloys can be combined within the Schottky diode structure to tailor the diode response to specific applications. Work is on-going to develop a high temperature electronic nose consisting of an array of appropriately tailored gas sensors based on SiC and other materials [3]. However, this work depends on the ability to package these sensors for the appropriate operating conditions. This paper discusses our on-going development of SiC-based gas sensors. First, the effect of the geometry of the insulator on the MRIS sensor behavior was studied. Second, a prototype sensor package allowing high temperature operation of the sensor in ambient conditions will be discussed.

2.0 Device Fabrication and Testing

The SiC-based sensors are fabricated from chips with a 4-5 μm thick alpha-SiC epilayer grown by chemical vapor deposition on a commercially available off-axis alpha-SiC substrate. A backside contact is achieved by sputtering aluminum onto the bottom of the wafer. The MRIS sensor investigated in this work is shown schematically in Figure 1b. A thin layer of approximately 50 angstroms (Å) of SnO_2 is sputter deposited onto half of the as-grown SiC epilayer surface (layer SnO_2 configuration). On both halves of the wafer, open circular patterns of 200 µm diameter were formed using photoresist. The SnO_2 layer half (left half of Figure 1b) of the wafer was then covered masking off the circular photoresist patterns; on the other half of the wafer 50 Å SnO_2 contacts (diode SnO_2 configuration) were formed by sputter deposition using the same parameters as the first SnO_2 deposition. The layer side was then uncovered and circular palladium (Pd) contacts approximately 400 angstroms (Å) thick were formed on both sides by sputter deposition and the subsequent lift-off. Thus, the SnO_2 is deposited completely across the surface (layered configuration on the left half of Figure 1b) on roughly half the chip while on the other half SnO_2 is deposited only beneath the Pd contact (diode configuration surface on the right half of Figure 1b). The difference between the two sides of the chip is the geometry of the SnO_2 layer beneath the Pd. This is in contrast to the previous tests (Figure 1a) where half the chip had the SnO_2 layer beneath the Pd and the other half had no SnO_2 at all beneath the Pd.

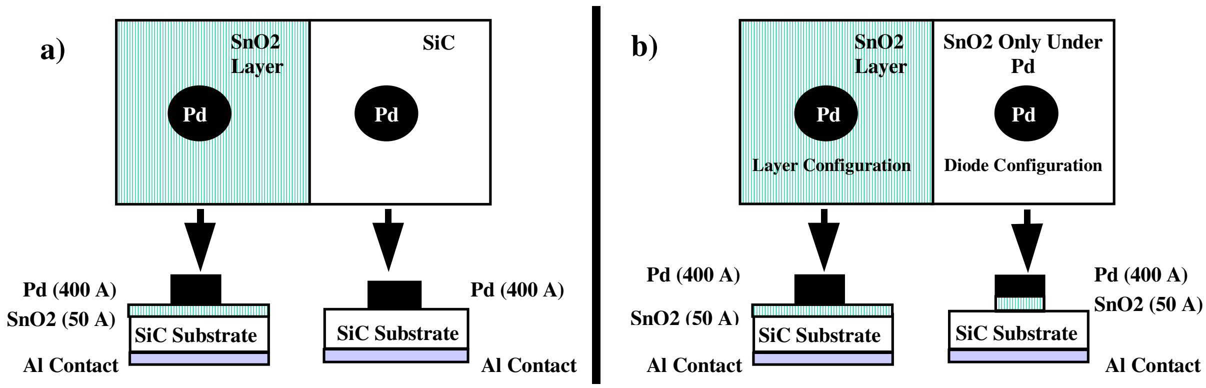

Figure 1: A schematic drawing of the test structures for: a) the MRIS approach which compared a Pd/SiC diode to a Pd/SnO_2/SiC diode. (Ref. 2) b) the effect of the reactive insulator (SnO_2) geometry on the sensor behavior of a Pd/SnO_2/SiC diode.

The gas sensor testing facility and sample connections have been described elsewhere [1]. The sample rested on a hot stage whose temperature is controlled from room temperature to 425 °C. Current-time (I-t) measurements were taken to characterize the diode response as a function of time during exposure to a variety of gases, and current-voltage (I-V) measurements were taken to characterize the diode's electronic properties in a given environment. The forward voltage at which the current is measured is chosen to maximize diode response and minimize series resistance effects.

3.0 Results and Discussion

3.1 Effects of Reactive Insulator Geometry

Heating the structures in Figure 1b at 350 °C for extended periods has shown a difference in behavior between the layer configuration sensors and diode configuration sensors (Figure 2). Both sensors are first exposed to air (10 minutes), nitrogen plus 10% oxygen (15 minutes), nitrogen plus 10% oxygen and 2500 ppm hydrogen, denoted as H_2 mix, (15 minutes), followed by nitrogen plus 10% oxygen (5 minutes) and air (10 minutes). The diode configuration sensor has nearly no response to H_2 at this concentration while the layer configuration sensor has a significant response. Comparison of the I-V curves of the two configurations is shown in Figure 3. The layer configuration sensor shows exponential behavior at low voltages and series resistance behavior at higher voltages. An increase in the current for a given voltage is noted upon exposure to H_2 for this sensor. However, the diode's H_2 sensitivity is less than that noted for the previously investigated Pd/SnO_2/SiC sensor with a layer SnO_2 configuration [2].

The diode configuration sensor shows complicated behavior as a function of voltage. In air, exponential I-V behavior is noted below 0.4 V. The slope of the exponential changes near 0.4 V and remains nearly constant from 0.4 to 2.5 V. The sensor does not respond to H_2 at this concentration below 1.5 V, while between from 1.5 to 2.5 volts a small response to H_2 is noted. Above 2.5 V, series resistance behavior is noted in both the air and H_2 mix curves. This sensor does not have the standard Schottky diode characteristics noted in Pd/SiC diodes previously investigated [1]. In contrast to the results of reference 2, the layer configuration sensor exhibits more standard Schottky diode behavior. Thus, the diode configuration sensor behavior is obviously different than that of the layer configuration sensor. These results suggest that the geometry of the reactive insulator, i.e. whether the SnO_2 covers the whole region around the sensor or just underneath the diode, affects the behavior of the sensor. The underlying reason for the effect will be investigated in future studies.

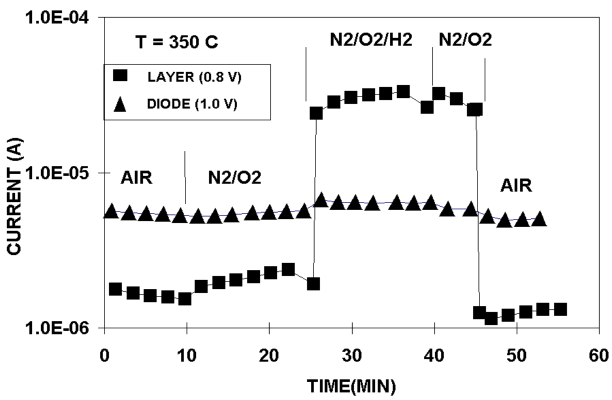

Fig.2. The forward current vs time at 350 °C upon exposure to H_2 mix of the layer configuration sensor and diode configuration sensor.

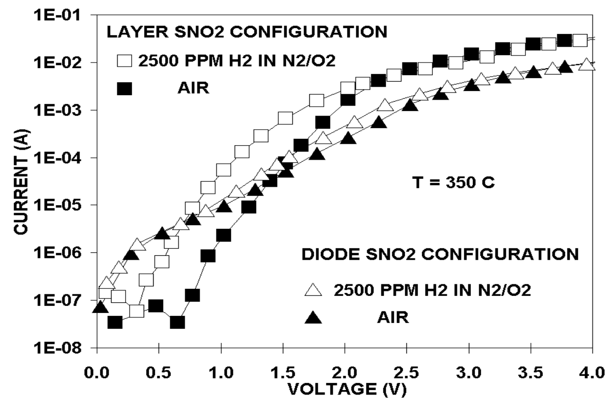

Fig.3. The logarithmic I-V curve at 350 °C in air and in the H_2 mix of the layer configuration sensor and diode configuration sensor.

These results have some similarities to those seen when comparing the Pd/SiC sensor to that of the Pd/SnO_2/SiC layer configuration sensor in reference 2. In both cases, increased sensitivity to H_2 is noted for sensors in the layer configuration compared to sensors without the layer. In summary, the diode sensitivity and stability is improved when the SnO_2 layer covers half the chip compared to that of a sensor where a SnO_2 layer does not extend beyond the boundary of the Pd contact.

The difference between the SnO_2 layer configuration sensors discussed in this work (diode 1) and in reference 2 (diode 2) is of interest. Both sensors show exponential behavior followed by series resistance behavior at higher voltages (not shown). The low voltage behavior in air of both diodes is shown in Figure 4 in a linear current scale. At lower voltages, diode 2 shows a linear I-V curve (shunt resistive behavior) until at least 0.6 V. The slope of the I-V curve gives an effective resistance of near $2*10^6$ Ω which is a value consistent with the resistance of a thin SnO_2 film. Above 0.9 V, diode 1 exhibits exponential behavior. In contrast, the I-V curve of diode 2 shows noise current below 0.8 V while above 0.8 V exponential behavior is observed. Thus, the most significant difference in the behavior of the two diodes is the shunt resistance behavior at lower voltages. These results suggest that differences in the deposition of a SnO_2 film can affect the sensor response even if the geometry of the film is the same. Possible differences in the SnO_2 film deposition parameters include thickness of the film and stoichiometry of the SnO_2.

3.2 Sensor Packaging

The ability to package a sensor for a given environment is of fundamental importance to its eventual application. One difficulty with operating sensors which function at higher temperatures than ambient is that a considerable amount of power (order of several watts) may be necessary to properly heat the sensor. For example, temperatures above 300-400 °C will likely be necessary to optimally measure gases such propylene and methane [1]. The heat power demand to achieve such temperatures may limit sensor use in some applications. Thus, the development of appropriate sensor packaging technology is necessary. Figure 5 shows the schematic of a prototype sensor package incorporating a Pd/SiC based sensor, temperature detector, and heater. The sensor resides on a micromachined diaphragm structure; this diaphragm structure minimizes the thermal mass and decreases the amount of power necessary to heat the sensor to appropriate temperatures. It also allows heating of the sensor with minimal heating of the adjoining package components. Temperatures up to 600 °C have been achieved with a heater power of near 1 W. Further, at approximately 500 °C, the packaged Pd/SiC sensor with a built-in heater has measured 5000 ppm of H_2, ethylene, and methane in N_2 (not shown). The methane signal has a longer response time than that of H_2 and ethylene, but has the same general shape of I-t curve. This is in contrast to the results at lower temperatures where the methane response was fundamentally different than the sensor response to H_2 and propylene [1]. However, as would be expected, degradation of the sensor response occurs with continued high temperature operation. This type of packaging can also be used for a variety of other sensors which would constitute the high temperature electronic nose.

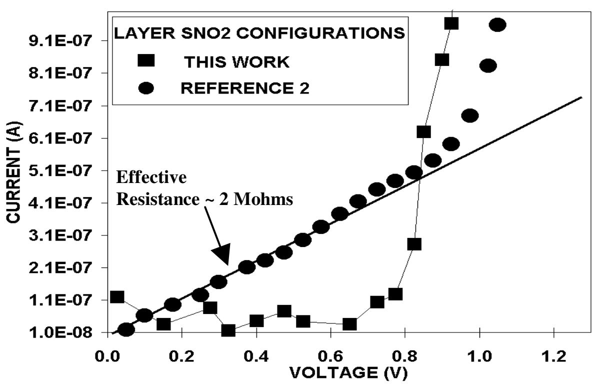

Fig. 4. The I-V curve in air on a linear current scale at 350 °C of the Pd/SnO_2/SiC diode in this work and in reference 2.

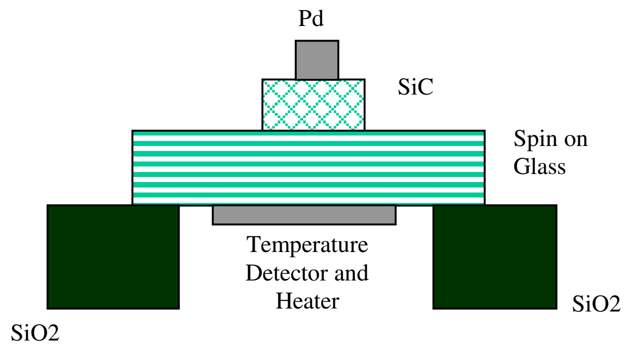

Fig. 5. Schematic drawing of sensor package for SiC-based devices.

4.0 Conclusions and Future Plans

The MRIS diode structure shows a dependence on the geometry of the insulator. Further studies with other diode geometries, reactive insulators, and processing conditions are planned. Integration of MRIS and metal alloy-SiC sensors together into an appropriate sensor package is also planned. By integrating SiC-based sensors with various structures into a sensor array, the sensor array can be tailored to meet the detection needs of a range of gas sensing applications.

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Silicon carbide based Schottky diode gas sensors are being developed for applications such as emission measurements and leak detection. The effects of the geometry of the tin oxide film in a Pd/SnO_2/SiC structure will be discussed as well as improvements in packaging SiC-based sensors. It is concluded that there is considerable versatility in the formation of SiC-based Schottky diode gas sensing structures which will potentially allow the fabrication of a SiC-based gas sensor array for a variety of gases and temperatures.

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